

PIEZOELECTRIC STRUCTURE,  
LIQUID EJECTING HEAD AND  
MANUFACTURING METHOD THEREFOR

5 FIELD OF THE INVENTION AND RELATED ART:

The present invention relates to a piezoelectric structure, a liquid ejecting head and a manufacturing method therefor.

10 Recently, printers using liquid ejection recording devices are widely used as printing apparatuses for personal computers or like, because of the high printing property, easy manipulation, low cost or the like. The liquid ejection recording devices are of a type in which a bubble is generated  
15 in liquid such as ink by thermal energy, and the droplet is ejected by the resulting pressure wave, a type in which the droplet is sucked and discharged by electrostatic force, a type in which a pressure wave is produced by a vibration element such as a  
20 piezoelectric element, or the like.

In a liquid ejecting apparatus using a piezoelectric element, there are provided a pressure chamber in fluid communication with a liquid supply chamber, a liquid ejection outlet in fluid  
25 communication with the pressure chamber, a vibrational plate of a piezoelectric element connected to the pressure chamber. With such a structure, a

predetermined voltage is applied to the piezoelectric element to collapse and expand the piezoelectric element, thus producing a vibration. This compresses the liquid in the pressure chamber and ejects the droplet through the liquid ejection outlet. Recently, a liquid ejecting apparatus is widely used, and the improvement in the printing property, particularly, the high resolution, the high speed printing, and/or long size liquid ejecting head are desired. To meet such demands, high resolution and high speed liquid ejecting head is tried, using a multi-nozzle head structure having high density nozzles. In order to increase the density, it is required to downsize the piezoelectric element for ejecting the liquid. It is desirable that manufacturing is completed through a semiconductor film formation process, from the some point of low cost with high precision, particularly in the case of the long liquid ejecting head.

However, the piezoelectric film is manufactured by forming  $PbO$ ,  $ZrO_2$  and  $TiO_2$  powder into a sheet, and then baking it, and therefore, it is difficult to produce a thin piezoelectric film such as not more than 10 $\mu m$ . Because of this, fine processing of the piezoelectric film is difficult, and this makes the downsizing of the piezoelectric element difficult. In the case that piezoelectric film is produced by baking the powder, the influence of the grain boundary

of crystalline is not negligible, and therefore, good piezoelectric particularly property cannot be provided. As a result, the piezoelectric film produced by baking the powder does not exhibit

5 satisfactory piezoelectric particularly property for ejecting the liquid such as ink in the thickness is not more than 10 $\mu$ m. For this reason, a small size liquid ejecting head having necessary properties for liquid ejection has not been accomplished.

10 The powder sheet is simultaneously baked on a vibrational plate and/or a structural member of ceramic or the like. With this, when a high density ceramic is intended, a dimension change due to contraction of the materials is not negligible. This

15 places a limit to a size, and it is difficult to arrange a great number of liquid ejection outlets (nozzles).

Japanese Laid-open Patent Application Hei 11-348285 proposes a structure and a manufacturing method

20 for a liquid ejecting head using a micro fabrication through a semiconductor process employing a sputtering method. In this publication, an orientatioal film formation of platinum is effected on a monocrystal MgO, and a layer of perovskite not comprising Zr layer

25 and PZT layer are laminated.

However, with the system, there arise the following problems:

(1) the single orientation crystal or monocrystal PZT are not stably produced with high reproducibility:

(2) the oriented PZT layer can be provided only on a monocrystal substrate of monocrystal MgO or the like which is expensive, and therefore, the process is very expensive. In addition, there is a limited in the size of the monocrystal substrate of MgO, and therefore it is not possible to produce a large area substrate.

(3) Using the method disclosed in this publication, the connection occurs in the neighborhood of the piezoelectric member or the connecting portion between the piezoelectric member and the member constituting the pressure chamber (liquid chamber) by adhesive material or the likes. In the region of micromachining, the reliability against the repetition of the stresses or the like is not sufficient.

(4) The vibrational plate in the method disclosed in the application, is directly contacted to the liquid such as ink in the liquid ejecting head, and in addition, in the manufacturing process, it is contacted to the acid, alkali or another chemical agent, and therefore, it is not possible to produce reliable liquid ejection elements. Moreover, the manufacturing process is complicated, and the liquid ejecting heads are expensive.

SUMMARY OF THE INVENTION:

Accordingly, it is a principal object of the present invention to provide a liquid ejecting head and a manufacturing method therefor, wherein a  
5 piezoelectric film, vibrational plate or the like constituting the piezoelectric element are made thin films, by which micro fabrication ordinarily used in the semiconductor process is usable, and a  
10 piezoelectric structure having a high durability and high piezoelectric particularly property with long size and high density of liquid ejection outlets.

According to an aspect of the present invention, there is provided a piezoelectric structure comprising: a vibrational plate; a piezoelectric film;  
15 said vibrational plate including a layer of a monocrystal material, a polycrystal material, a monocrystal material doped with an element which is different from an element constituting the monocrystal material, or a polycrystal material doped with an  
20 element which is different from an element constituting the polycrystal materials, and oxide layers sandwiching the aforementioned layer; said piezoelectric film has a single orientation crystal or monocrystal structure.

25 According to another aspect of the present invention, there is provided a manufacturing method for manufacturing a piezoelectric structure having a

vibrational plate and a piezoelectric film, said method comprising: a step of forming a second oxide layer on a silicon substrate having a monocrystal silicon layer on a silicon layer with an oxide layer interposed therebetween; a step of forming a piezoelectric film of a single orientation crystal or monocrystal structure on the second oxide layer; and a step of an upper electrode on the piezoelectric film.

According to a further aspect of the present invention, there is provided a liquid ejecting head comprising a liquid ejection outlet; a main assembly substrate portion having a pressure chamber in fluid communication with said liquid ejection outlet and having an opening; a piezoelectric structure connected so as to plug the opening; said piezoelectric structure including, a vibrational plate; a piezoelectric film; said vibrational plate including a layer of a monocrystal material, a polycrystal material, a monocrystal material doped with an element which is different from an element constituting the monocrystal material, or a polycrystal material doped with an element which is different from an element constituting the polycrystal materials, and oxide layers sandwiching the aforementioned layer, said piezoelectric film has a single orientation crystal or monocrystal structure.

According to a further aspect of the present

invention, there is provided a manufacturing method for a liquid ejecting head including a liquid ejection outlet; a main assembly substrate portion having a pressure chamber in fluid communication with said liquid ejection outlet and having an opening; a piezoelectric structure connected so as to plug the opening, said manufacturing method comprising: a step of forming a second oxide layer on a silicon substrate having a monocrystal silicon layer on a silicon layer with an oxide layer interposed therebetween; a step of forming a piezoelectric film of a single orientation crystal or monocrystal structure on the second oxide layer.

According to the present invention, the vibrational plate constituting the piezoelectric structure and having a monocrystal or polycrystal structure is sandwiched by oxide materials, so that even if fine cracks are produced as a result of repetition of mechanical displacement, the strength of the vibrational plate per se is maintained, and the adhesiveness relative to the piezoelectric film is not deteriorated, and therefore, durable devices can be provided.

In addition, a piezoelectric film of single orientation crystal or monocrystal having a high piezoelectric constant can be formed on the silicon substrate, and therefore, a film having a uniform

crystal orientation can be sequentially formed on the substrate, so that piezoelectric structure having high frequency property, durability and electrostrictive / piezoelectric property, can be produced.

5           By incorporating such a piezoelectric structure, a device having a high durability, high density, large ejection power with high frequency, in which the performance of each of the liquid ejection outlets are uniform can be provided. In addition, by  
10   producing the piezoelectric member and the vibrational plate or the like as thin films, the micro fabrication usable in the semiconductor process is available. In addition, a liquid ejecting head having a high  
15   durability, electrostrictive / piezoelectric particularly property, a large length, a stabilized reliability, can be provided.

#### BRIEF DESCRIPTION OF THE DRAWINGS:

20           Figure 1 is a perspective view of a liquid ejecting head according to an embodiment of the present invention (a), and a sectional view thereof taken on a line A-A.

          Figure 2 is a partially sectional view of a piezoelectric structure usable for a liquid ejecting  
25   head according to the embodiment of the present invention.

          Figure 3 is a partially sectional view of a



piezoelectric structure manufactured on the basis of a manufacturing method according to an embodiment of the present invention.

5 Figure 4 is a partially sectional view of a liquid ejecting head manufactured on the basis of a manufacturing method according to an embodiment of the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS:

10 The description will be made as to the preferred embodiment of the present invention in conjunction with the accompanying drawings.

15 In Figure 1, (a) is a perspective view of a liquid ejecting head according to an embodiment of the present invention, and (b) is a sectional view taken along a line A-A in (a). Figure 2 is a partially sectional view of a piezoelectric structure usable for a liquid ejecting head according to the embodiment of the present invention.

20 As shown in Figure 1, the liquid ejection recording head 1 in this embodiment comprises a plurality of liquid ejection outlets (nozzles) 2, a plurality of pressure chambers (liquid chambers) 3, a piezoelectric structure 10 provided for each of the  
25 pressure chambers 3. The liquid ejection outlets 2 are formed in the orifice plate 5 at predetermined intervals. The pressure chamber 3 is formed in the

main assembly substrate portion (liquid chamber  
substrate) 6, corresponding to the liquid ejection  
outlet 2. The pressure chamber 3 as are connected to  
the respective liquid ejection outlets 2 through the  
5 liquid flow paths 6a. In this embodiment, the liquid  
ejection outlets 2 are provided on the bottom side,  
the they may be provided on the lateral side. On the  
top side of the main assembly substrate portion 6, an  
opening 6b is formed corresponding to each of the  
10 pressure chamber 3, and the piezoelectric structure 10  
is positioned so as to plug the opening 6b on the top  
side of the main assembly substrate portion 6. The  
piezoelectric structure 10 comprises a vibrational  
plate 11 and a piezoelectric element 12.

15 The vibrational plate 11 constituting the  
piezoelectric structure 10 of this embodiment, as  
shown in Figure 2, comprises monocrystal material or  
polycrystal material, which is sandwiched by a first  
oxide layer 13 and a second oxide layer 14. The  
20 piezoelectric film 15 of the piezoelectric element 12  
constituting the piezoelectric structure 10 is made of  
single orientation crystal or monocrystal material.  
On the top and bottom sides thereof, there are formed  
electrodes 16, 17 of Au, Pt one like. The  
25 piezoelectric element 12 is constituted by the  
piezoelectric film 15 and the electrodes 16, 17.

By constituting the piezoelectric structure

10 in this manner, the vibrational plate 11 of the monocrystal polycrystal structure is sandwiched by the oxides 13, 14, and therefore, despite repeated mechanical displacements with the result of fine cracks, the vibrational plate per se is not damaged, and the adhesiveness relative to the piezoelectric film is not deteriorated. Thus, the durability is high.

As to the vibrational plate 11, and the first oxide layer 13 at the side remote from the piezoelectric film 15 and the second oxide layer 14 at the piezoelectric film 15 side, with the vibrational plate 11 interposed therebetween, the film thicknesses are selected so as to satisfy  $d_1 + d_2 \leq D_1$ , where  $D_1$  is a film thickness of the vibrational plate 11,  $d_1$  is a film thickness of the first oxide layer 13, and  $d_2$  is a film thickness of the second oxide layer 14. When this is satisfied, the durability is further improved in the piezoelectric structure (10) and the liquid ejecting head (1).

More specifically, the film thicknesses of the vibrational plate 11 (film thickness  $D_1$ ), the first oxide layer 13 (film thickness  $d_1$ ), second oxide layer 14 (film thickness  $d_2$ ) are  $d_1 = 5\text{nm} - 5\mu\text{m}$ , preferably  $10\text{nm} - 3\mu\text{m}$ . The film thickness  $d_2$  is  $5\text{nm} - 3\mu\text{m}$ , preferably  $10\text{nm} - 1\mu\text{m}$ . Film thickness  $D_1$  is  $100\text{nm} - 10\mu\text{m}$ , preferably  $500\text{nm} - 5\mu\text{m}$ . If the film thickness

D1 of the vibrational plate 11 exceeds 10 $\mu$ m, the degree of displacement becomes insufficient for a liquid ejecting head, and therefore, it is not preferable for the high density nozzle arrangement.

5 In this embodiment of the piezoelectric structure,  $d_1+d_2+D_1 \leq 5 \times D_2$  is preferably satisfied, where D2 is a film thickness of the piezoelectric film 15. When  $d_1+d_2+D_1 \leq 5 \times D_2$  is satisfied, the degree of displacement in the piezoelectric structure is large enough. The specific film thickness D2 of the  
10 piezoelectric film 15 is 500nm -10 $\mu$ m, preferably 1 $\mu$ m - 5 $\mu$ m.

The material of the vibrational plate 11 is Si, preferably monocrystal Si. The vibrational plate  
15 11 may be doped with element such as B. The grating constant of the Si used for vibrational plate 11 may be used to provide the piezoelectric film 15 of single orientation crystal or monocrystal.

The material of the first oxide layer 13  
20 formed on upper may be SiO<sub>2</sub>, YSZ, (yttrium-stabilized zirconia), MgO or the like, and the material of the second oxide layer 14 may be at least one of SiO<sub>2</sub>, YSZ, Al<sub>2</sub>O<sub>3</sub>, LaAlO<sub>3</sub>, Ir<sub>2</sub>O<sub>3</sub>, MgO, SRO(SrRuO<sub>3</sub>) STO(SrTiO<sub>3</sub>) or the like. When the use is made with an  
25 oxide other than SiO<sub>2</sub>, the material has a crystal orientation (111) or (100). When the oxide layer is a combination of SiO<sub>2</sub> and another oxide, a small amount

of metal element of said another oxide may be contained to provide a preferable vibration property or the like of the vibrational plate. The content is not more than 10at%, preferably not more than 5at%.

5           The material of the piezoelectric film 15 to be used for the piezoelectric structure 10 according to this embodiment may be, for example:  
PZT[Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub>], PMN[Pb(Mg<sub>x</sub>Nb<sub>1-x</sub>)O<sub>3</sub>],  
PNN[Pb(Nb<sub>x</sub>Ni<sub>1-x</sub>)O<sub>3</sub>], PSN[Pb(Sc<sub>x</sub>Nb<sub>1-x</sub>)O<sub>3</sub>],  
10 PZN[Pb(Zn<sub>x</sub>Nb<sub>1-x</sub>)O<sub>3</sub>], PMN-PT{(1-y)[Pb(Nb<sub>1-x</sub>)O<sub>3</sub>]-  
y[PbTiO<sub>3</sub>]}, PSN-PT{(1-y)[Pb(Sc<sub>x</sub>Nb<sub>1-x</sub>)O<sub>3</sub>]-y[PbTiO<sub>3</sub>]},  
PZN-PT{(1-y)[Pb(Zn<sub>x</sub>Nb<sub>1-x</sub>)O<sub>3</sub>]-y[PbTiO<sub>3</sub>]}. Here, x and  
y are not more than 1 and not less than 0. For  
example, in the case of PMN, x is preferably 0.2-0.5;  
15 and in the case of PSN, x is preferably 0.4-0.7; in  
the case of PMN-PT, y is preferably 0.2-0.4; in the  
case of PSN-PT, y is preferably 0.35-0.5; in the case  
of PZN-PT, y is preferably 0.03-0.35.

20           In this embodiment, these materials can be formed into a single orientation crystal or monocrystal film, and therefore, the performance is high. For example, as a method of providing a piezoelectric film having a monocrystal structure through a sputtering film formation method, a rapid  
25 cooling from the film formation temperature as a rate of not less than 30°C /min. Another method is usable.

The piezoelectric film may have a further

structure of a single composition, or may be a laminated structure of two or more compositions. For the pulse of crystalline structure control, the film formation may be carried out after film formation of the anchoring layer of different material compositions. For example, in the case of monocrystal film formation of PZT, Zr component tends to enter at the initial stage, and therefore, the film formation thereof is preferably carried out after the film formation of the anchoring layer of  $\text{PbTiO}_3$ . It may be a composition doped with a small amount of element in the main component. The single orientation crystal or the monocrystal has a priority orientation degrees of the film of not less than 80%, preferably not less than 85%, and further preferably not less than 95%, as determined by XRD (X-ray diffraction apparatus) ( $\theta - 2\theta$  (out of plane) measurement).

An example in which the monocrystal piezoelectric film of PMN-PT or PZN-PT is used as a piezoelectric element is disclosed in US Patent No.5804907, in which a bulk of crystal member produced through TSSG method (Top Speeded Solution Growth method) is cut and then is connected to the substrate (vibrational plate). This method is not suitable for a micro fabrication, and it is not possible to provide a film thickness of the piezoelectric film not more than  $10\mu\text{m}$ . In addition, it is necessary to cut along

the orientation of the crystal in the bulk, which is cumbersome and time-consuming, and there is a probability of erroneous alignment with the crystal orientation.

5           According to this embodiment, a film having a sequentially aligned crystal orientation can be formed on the substrate, and therefore, such programs do not arise. In the case of the liquid ejecting head, the variations of the ejection performance is small, and  
10           the connection strength is high. In addition, the film is a piezoelectric film of single orientation crystal or monocrystal, and therefore, the durability and the piezoelectric particularly property are preferable.

15           Specific layer structures of the piezoelectric structure according to this embodiment will be described. The display of the layer structure is "upper electrode 17// piezoelectric film 15// lower  
20           electrode 16// second oxide layer 14// vibrational plate 11// first oxide layer 13" (reference numerals are as shown in Figure 2).

Example 1:

Pt//PZT(001)//PT(001)//Pt(100)//MgO(100)//Si(100)//SiO<sub>2</sub>

25           The vibrational plate with this layer structure is Si(100), and the oxide layers sandwiching the vibrational plate is MgO(100) and SiO<sub>2</sub>. The following is other examples:

Example 2:

Au//PZT(001)/PT(001)//PT(100)//YSZ(111)/SiO<sub>2</sub>//Si(111)//SiO<sub>2</sub>

Example 3:

Au//PZT(111)/PT(111)//PT(111)//YSZ(100)/SiO<sub>2</sub>//Si(100)//SiO<sub>2</sub>

5

Example 4:

Pt//PZT(111)/PT(111)//Pt(111)//YSZ(100)/Zr//Si(100)//SiO<sub>2</sub>

Example 5:

Pt//PZT(111)/PT(111)//Pt(111)//MgO(111)//Si(100)//SiO<sub>2</sub>

Example 6:

10 Au//PZT(001)//SRO(001)//Si(100)//SiO<sub>2</sub>

Example 7:

Al//PZT(111)//SRO(111)//Si(111)//SiO<sub>2</sub>

Example 8:

Au//PZT(111)/PT(111)//Pt(111)//YSZ(100)/SiO<sub>2</sub>//Si(100)//YSZ(100)

15

Example 9:

Pt//PZT(001)//SRO(001)//Si(100)//YSZ(100)

Example 10:

Au//PZT(001)/PT(001)//Pt(100)//MgO(100)//Si(100)//YSZ(100)

Example 11:

20 Pt//PZT(001)/PT(001)//Pt(100)//MgO(100)//Si(100)//YSZ(100)

Example 12:

Pt//PZT(001)/PT(001)//Pt(100)//Al<sub>2</sub>O<sub>3</sub>(100)//Si(100)//SiO<sub>2</sub>

Example 13:

Ag//PZT(001)/PT(001)//Pt(100)//LaAlO<sub>3</sub>(100)//Si(100)//SiO<sub>2</sub>

25

In examples 6, 7 and 9, SRO has a director conductivity, and it also functions as the second oxide layer 14 and the lower electrode 16. In the



foregoing examples, the piezoelectric film is of a laminated structure of PZT for PZT/PT. The structure may be replaced with the layer structure of PMN, PZN, PSN, PNN, PMN-PT, PSN-PT, PZN-PT.

5 For example, the followings are usable alternatives:

Au//PMN(001)//Pt(100)//MgO(100)//Si(100)//SiO<sub>2</sub>;  
Pt//PMN-

PT(001)//Pt(100)//MgO(100)/SiO<sub>2</sub>//Si(100)//SiO<sub>2</sub>;

10 Al//PMN-

PT(001)/PT(001)//Pt(100)//YSZ(111)/SiO<sub>2</sub>//Si(111)//SiO<sub>2</sub>

The crystal orientations indicated in the parentheses in the layer structure indicate the crystal orientation having priority orientation not less than 80%, preferably not less than 85%, other preferably not less than 95%, as described hereinbefore.

As for the second oxide layer 14, the SiO<sub>2</sub> which is a Si oxide film or another oxide (YSZ, MgO, Ir<sub>2</sub>O<sub>3</sub>) may be selected depending on the manufacturing process. For example, it is possible to suppress production of SiO<sub>2</sub> by forming a YSZ film using the metal target during the film formation of the YSZ. By thin film formation of metal such as Zr or the like on the Si layer, the production of SiO<sub>2</sub> can be prevented.

The description will be made as to the

manufacturing method of the piezoelectric structure and the liquid ejecting head according to the embodiment of the present invention.

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The manufacturing method for the  
5 piezoelectric structure having the vibrational plate and the piezoelectric film according to this embodiment comprises a step (1) of forming a second oxide layer on a silicon substrate having a  
monocrystal silicon layer on a silicon layer with an  
10 oxide layer interposed therebetween; a step (2) of forming a piezoelectric film of a single orientation crystal or monocrystal structure on the second oxide layer; and a step (3) of an upper electrode on the piezoelectric film.

15 Another manufacturing method for a liquid ejecting head including a liquid ejection outlet; a main body substrate portion having a pressure chamber in fluid communication with said liquid ejection outlet and having an opening; a piezoelectric  
20 structure connected so as to plug the opening, according to the present invention comprises, in addition to the steps (1) -(3), a step (4) of separating the piezoelectric film into a plurality of portions; a step (5) of an upper electrode on the  
25 piezoelectric film; a step (6) of forming said pressure chamber.

Each of these steps will be described. In

the step (1) the silicon substrate having the monocrystal silicon layer above the silicon layer with the oxide layer therebetween may be SOI (silicon-on-insulator) substrate, or a film of monocrystal oxide may be formed on the silicon substrate, and a film of monocrystal silicon layer may be formed thereon. In the case of SOI substrate, the oxide layer on the silicon layer is  $\text{SiO}_2$ , for example, and the monocrystal oxide is YSZ(100), YSZ(111),  $\text{MgO}(100)$ ,  $\text{MgO}(111)$ ,  $\text{STO}(100)$ ,  $\text{STO}(111)$  or the like, for example. The film thickness (d1) of the oxide layer is 5nm - 5 $\mu\text{m}$ , preferably 10nm - 3 $\mu\text{m}$ . These oxide layers are usable as an etching stop layer in the step (5) of forming a pressure chamber.

The second oxide layer formed on the monocrystal silicon is preferably formed prior to the step (2) and/or step (3). The second oxide layer may be  $\text{SiO}_2$ , YSZ(100), YSZ(111),  $\text{SRO}(001)$ ,  $\text{SRO}(111)$ ,  $\text{MgO}(100)$ ,  $\text{MgO}(111)$ ,  $\text{Ir}_2\text{O}_3(100)$ ,  $\text{Ir}_2\text{O}_3(111)$ ,  $\text{Al}_2\text{O}_3(100)$ ,  $\text{Al}_2\text{O}_3(111)$ ,  $\text{LaAlO}_3(100)$ ,  $\text{LaAlO}_3(111)$ ,  $\text{STO}(100)$ ,  $\text{STO}(111)$  or the like, for example. The film thicknesses (d2) of them, are 5nm - 3 $\mu\text{m}$ , preferably 10nm - 1 $\mu\text{m}$ .

In the above-described layer structure, the second oxide layer is  $\text{MgO}$  in example 1, and YSZ and  $\text{SiO}_2$  in example 2. The  $\text{SiO}_2$  may be produced by oxidative reaction during YSZ film formation which is

a buffering film, or maybe produced by heat treatment after the film formation. When the second oxide layer contains  $\text{SiO}_2$ , it is preferable that small amount of the medal of another oxide layer (buffering film) is contained in the  $\text{SiO}_2$ , and the method therefor is preferably a sputtering method using an oxide target as the film formation method for another oxide layer. The film thickness of  $\text{SiO}_2$  layer can be controlled by selecting the temperature lowering process from maximum temperature of the formed YSZ film, a temperature maintaining duration thereof, a re-heat-treatment condition and a temperature maintaining duration thereof. For example, the film thickness of the  $\text{SiO}_2$  layer can be increased by the sputtering film formation temperature being maintained in the water vapor atmosphere. The production of the  $\text{SiO}_2$  layer at the interface between the YSZ and the Si may be prevented by first forming a metal layer using the metal Zr target and then forming a film of YSZ. It can be selected depending on the material and the performance whether the  $\text{SiO}_2$  layer is to be formed or not.

In the step (2), a piezoelectric film having a single layer structure or a laminated structure is formed, using any of composition such as PZT, PMN, PZN, PSN, PNN, PMN-PT, PSN-PT, PZN-PT or the like. The piezoelectric film preferably has a single

orientation crystal or monocrystal structure.

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The formation of the upper electrode on the piezoelectric film in the step (3), may be effected through a sputtering method, an evaporation method, an application method or the like. The electrode material may be a metal material such as Au, Pt, Cr, Al, Cu, Ir, Ni, or an electroconductive oxide such as SRO, ITO. The upper electrode may be a solid electrode or a comb-shaped electrode on the piezoelectric film.

In the manufacturing method for the piezoelectric structure, according to the embodiment of the present invention, it is possible that single orientation crystal or monocrystal piezoelectric film having a high piezoelectric constant can be formed on the silicon substrate, and therefore, a vibrational plate in which the connection strength, the durability is high, can be produced. Thus, a piezoelectric structure having a high frequency property, durability and electrostrictive / piezoelectric property can be provided.

In the manufacturing method for the liquid ejecting head, the step of separating the piezoelectric film in step (4) is a patterning step in which the piezoelectric film produced by the step (2). The patterning is separated corresponding to the liquid ejection outlets (nozzles) and the pressure

chambers. The patterning method may be a wet etching type, a dry etching type, a mechanical cutting type or like. In the case of the wet etching and dry etching types, a protecting film formation may be carried out for the protection of the silicon substrate with the resist treatment for the patterning. In addition, a resin material or the like having a low rigidity not preventing expansion and contraction of the piezoelectric film may be filled between the separated piezoelectric film.

The step (5) for forming the pressure chamber includes a process step for the silicon layer at the opposite side and/or a step of connecting a separate substrate having a formed pressure chamber portion with the silicon substrate. The process step for the silicon layer may be carried out through wet etching, dry etching, mechanical process (sandblast process or like). The substrate for said separate substrate having the pressure chamber portion may be a silicon substrate, a SUS substrate, a polymer material substrate or the like. The connecting method in the case of use of the silicon substrate, the SUS substrate or the like may be an anodic oxidation connection method, active metal soldering method or a method using an adhesive material. When a polymer material is used, etching process with the use of resist material is usable. Alternatively, a substrate

preprocessed is usable. The configuration of the pressure chamber may be rectangular, circular, elliptical or the like. In addition, in the case of side shooter, the cross-sectional configuration of the pressure chamber may be reduced toward the nozzle.

The step (6) of forming the liquid ejection outlet may include connecting an orifice plate in which the liquid ejection outlets are formed corresponding to respective pressure chamber portions, or forming the liquid ejection outlets from resist material or the like. Alternatively, after the polymer substrate is laminated, the liquid ejection outlets may be formed corresponding to the pressure chambers by laser machining. In the case of the formation of the liquid ejection outlets using a resist material, the forming operation may be carried out simultaneously with the step (5). The order of the steps (4), (5) and (6) is not limiting, and the separating step of the piezoelectric film (4) may be carried out finally.

According to the manufacturing method for the liquid ejecting head in this embodiment of the present invention, similarly to the case of the above-described piezoelectric structure, the piezoelectric film has a single orientation crystal or monocrystal structure, and therefore, the resultant vibrational plate has a high connection strength and durability,

and therefore, it is possible to provide a liquid ejecting head having a high density, a large ejection power and a suitability to a high frequency printing.

The description will be made as to specific examples.

(Example 1)

Referring to Figure 3, an example will be described. Figure 3 is a partially sectional view of a piezoelectric structure manufactured through a method for manufacturing the piezoelectric structure according to an embodiment of the present invention. A YSZ (100) 24 film having a thickness of  $0.3\mu\text{m}$  was formed on a monocrystal Si layer under  $800^{\circ}\text{C}$  through the sputtering film formation, using a SOI substrate constituted by a silicon layer 28 having a thickness of  $625\mu\text{m}$ , a  $\text{SiO}_2$  layer 23 having a thickness of  $0.2\mu\text{m}$  and a monocrystal Si(100) layer 21 having a thickness of  $3\mu\text{m}$ . Thereafter, a lower electrode Pt(111) 26 was formed into a thickness of  $0.5\mu\text{m}$ , and a piezoelectric film 22 of PT(111), PZT(111) was formed under  $600^{\circ}\text{C}$ . The composition of PZT was  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ . The total film thickness of the piezoelectric film 22 was  $3.5\mu\text{m}$ . In all of the film formation steps, the temperature rising speed in the cooling process after the film formation was not less than  $40^{\circ}\text{C}/\text{min}$ . To control the single crystal property of the film. By the step,  $0.02\mu\text{m}$  thick  $\text{SiO}_2$



layer 24a was formed as the second oxide layer at the interface between the YSZ(100) 24 and Si(100) 21. The film thickness of the SiO<sub>2</sub> layer 24a was 0.2μm in the case that it was formed under 800°C, and then it was maintained as it is in the water vapor for 100 min. The contents of Y and Zr metal in the SiO<sub>2</sub> was 4.6at%. The single crystal property of the piezoelectric film 22 had not less than 99% orientation of (111) as a result of confirmation by XRD (X line diffraction apparatus).

On the piezoelectric film 22, upper electrode 27 of Au was evaporated. Thereafter, a silicon layer 28 was etched into a rectangular configuration having a width 100μm and a length 2mm at the first oxide layer 23 by wet etching using TMAH (trimethylammonium hydroxide).

From the piezoelectric structure (Figure 3) manufactured in the above-described steps, the upper and lower electrodes 26, 27 are taken out, and the displacement was measured at driving frequency of 35kHz and driving voltage of +5V/-5V and was 0.26μm at the central portion. In the case of the structure having a 1.0μm thick second oxide layer 24, the preferable displacement of 0.25μm was measured.

A piezoelectric structure having the same structures except that piezoelectric film was a polycrystal member having an orientation property of

43% was manufactured, and the displacement was 0.04 $\mu$ m. The variations were significant, and the durability was low.

(Example 2)

5           Using a substrate in which the monocrystal Si layer has a crystal orientation (111), the sputtering film formation was carried out to manufacture the structure of example 2 in the above-described layer structure. By using a crystal orientation (001) of  
10 PZT, the durability was further improved. The displacement measured after the etching process similarly to Embodiment 1, was 0.25 $\mu$ m -0.28 $\mu$ m which were preferable.

(Example 3)

15           Referring to Figure 4, the description will be made as to the manufacturing method for the liquid ejecting head according to this example. Figure 4 is a partially sectional view of a liquid ejecting head manufactured through the manufacturing method  
20 according to the embodiment of the present invention.

          A MgO(100) 34 layer was formed into a thickness of 0.3 $\mu$ m on a monocrystal Si(100) 31 having been B-doped, using a substrate 39 of a B-doped monocrystal Si(100)/SiO<sub>2</sub>/Si structure (film  
25 thicknesses were 2.5 $\mu$ m/1 $\mu$ m/250 $\mu$ m). Furthermore, 0.4 $\mu$ m thick of Pt(100) and a piezoelectric film 32 of PMN(001) were formed into a thickness of 2.3 $\mu$ m. The

composition of the PMN was adjusted by  
Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>. TEM observation has confirmed that  
SiO<sub>2</sub> layer 34a of 0.05μm thick is formed at the  
interface between the MgO<sub>3</sub>4 and the Si(100) 31. On the  
5 upper electrode 37, Au was pasted. The Si layer 38  
was subjected to a plasma etching process using C4 F8  
to form the pressure chamber 41. Thereafter, the Si  
middle substrate 42 and the orifice plate 43  
constituting the pressure chamber were connected to  
10 provide the liquid ejecting head of this embodiment.

Figure 4 shows the liquid ejecting head  
manufactured through the method of this example, in  
which designated by 31 is a vibrational plate of B-  
doped monocrystal Si; 32 is a piezoelectric film of  
15 PMN; 33 is a first oxide layer; 34, 34a are second  
oxide layer; 36 lower electrode; and 37 is upper  
electrode. Designated by 38 is a Si layer in which  
the pressure chamber 41 is formed; 42 is a middle  
substrate; 43 is an orifice plate in which the liquid  
20 ejection outlets 44 are formed. The pressure chamber  
41 has a width of 60μm, a depth of 2.2mm, and a  
partition width between the adjacent pressure chambers  
41 of 24μm.

Using the liquid ejecting head, the ink  
25 ejection tests were carried out. A maximum ejection  
speed of /sec was confirmed at a driving frequency of  
35kHz with a driving voltage of +7V/-7V. The size of

the droplets was controllably 3pl - 26pl. Durability test repeating  $10^9$  displacements was carried out, and the decrease of the displacement was not more than 5%.

Two liquid ejecting heads were manufactured with the same structure except for the film thickness of the monocrystal silicon layer being 10 $\mu$ m and 11 $\mu$ m. The displacement in the liquid ejecting head having the Si layer of 10 $\mu$ m thick was smaller by 10% than the liquid ejecting head having the Si layer of 2.5 $\mu$ m thick, but could eject high viscosity(10cps) droplets. In the case of the liquid ejecting head using 11 $\mu$ m, the reduction of the displacement was 17%, but it could eject the high viscosity droplets, similarly. However, the durability is slightly lower than the liquid ejecting head using 10 $\mu$ m.

(Example 4)

The piezoelectric film in Embodiment 3 was modified by using a piezoelectric film of PSN-PT(001) (the other structures were the same). The composition of PSN-PT was suggested to be  $0.55[\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3] - 0.45[\text{PbTiO}_3]$ . The dimensions such as the width of the pressure chamber or the like were the same as in Embodiment 3. It was confirmed that ink could be ejected at a speed of 14.3m /sec with the same driving conditions. In addition, when the width of the pressure chamber was changed to 40 $\mu$ m, and the length of the pressure chamber was changed to 2.5mm, and the

ink could be ejected at a speed of not less than 10m /sec which is practical.

(Example 5)

5 The piezoelectric film in Embodiment 4 was changed to PZN-PT(001), without changing the other structures, and the liquid ejecting head was manufactured. The composition of PZN-PT was 0.90{Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>}-0.10{PbTiO<sub>3</sub> }. The ejection speed of the ink with the width of the pressure chamber being 60μm was 14.1m /sec which was 10 preferable. The quantities of the droplets were very stable.

While the invention has been described with reference to the structures disclosed herein, it is 15 not confined to the details set forth and this application is intended to cover such modifications or changes as may come within the purpose of the improvements or the scope of the following claims.

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